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(54) HYDROGENATION PROCESS AND CATALYST

(71) We, UNION OIL COMPANY OF CALIFORNIA, a corporation organised and existing under the laws of the State of California, United States of America, of 461 South Boylston Street, City of Los Angeles, County of Los Angeles, State of California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a catalyst having activity for the hydrogenation of aromatic hydrocarbons and to a process for hydrogenating aromatic hydrocarbons utilizing the catalyst.

There is today in the petroleum industry a steadily increasing demand for relatively non-aromatic middle distillate products boiling in the range of about 300°—700°F. Such products include for example aviation turbine fuels, diesel fuels and solvents. Products in this boiling range are conventionally produced by the hydrotreating and/or hydrocracking of various refinery streams boiling in or above the desired product range. Hydrotreating and hydrocracking operations generally effect a substantial partial hydrogenation or polycyclic aromatics, but the resulting products still contain a relatively high percentage of monoaromatic hydrocarbons. Further hydrogenation of these products is desired in many cases, for example to produce acceptable solvent products, or to meet specifications (smoke point and luminometer number) for jet fuels. The most active catalysts presently available for effecting this type of saturation are the noble metals, particularly platinum or palladium.

In view of the high cost of the noble metals, it is essential to use as little of such metal as possible. Efficient utilization of the metal requires a very high dispersion thereof, which explains the conventional approach of impregnating the metal salts upon high surface area supports such as alumina and silica gel. However, conventional impregnation

techniques rarely give more than about a 25 percent dispersion, defined as the ratio of surface (or available) metal to total metal present. 50

Recently, various ion-exchange procedures have been suggested as a means for obtaining a higher metal dispersion on zeolitic supports. Zeolitic supports however present an element of undesirability in connection with hydrogenation processes in which acid catalyzed reactions such as cracking and isomerization are undesired, inasmuch as the ion exchange sites on the support are potential acid centres which catalyze these undesired reactions. We have now found certain alumina-silica gel composites which possess sufficient ion-exchange capacity to combine with the desired amount of noble metal for hydrogenation purposes, but which after drying such ion-exchange sites are either destroyed or so weakened that little or no cracking activity is apparent in the final catalyst when utilized at hydrogenation temperatures below about 700°F. The metal component however remains in a high state of dispersion, generally amounting to at least 35—40 percent, as above defined. The resulting catalysts hence display an optimum intrinsic combination of hydrogenation activity with little or no cracking activity. 75

However, maximum metal dispersion on the support represents only one parameter of economy in metal utilization. The other major factor to be considered is availability of the dispersed metal. Depending upon the type of feedstock employed, the reaction temperature, the catalyst particle size, and the pore characteristics of the support, diffusion limitations may render a substantial portion of the noble metal relatively unavailable. Diffusion limitations can be overcome by utilizing finely powdered catalysts in fluidized or slurry type operations, but such contacting procedures are considerably more expensive than simple continuous flow, fixed-bed operations. But in fixed bed operations excessive pressure drops through the catalyst bed are encountered when catalyst particle size is reduced below about 80 90 95

[Price 25p]

1/32—1/16 inch in diameter.

It has now been found that in low-temperature hydrogenations (normally liquid phase), utilizing granular catalysts of suitable size for fixed-bed operation, and wherein the noble metal is highly dispersed as herein, the pore volume and pore size characteristics of conventional supports such as silica gel or activated alumina are such that the catalyst granules are severely diffusion limited, resulting in inefficient utilization of the highly dispersed noble metal in the interior of the catalyst granules. We have now found however that alumina-silica supports can be improved in these respects if they have an unusually high pore volume, and even more importantly a pore size distribution comprising a substantial volume of pores of diameter greater than 500 Å. The pore volume of conventional activated alumina supports normally falls in the range of 0.6—0.8 ml/gm, giving an apparent bulk density of 0.6—0.7 gms/ml, with only about 5—6 percent of the total pore volume being in pores of greater than 500 Å diameter. In contrast, the supports of the present invention have pore volumes in the range of 0.8—2.0 ml/gm, with typical bulk densities ranging from 0.2—0.6 gms/ml, and normally at least 20 percent of the total pore volume comprising pores of greater than 500 Å diameter. The use of these high pore volume supports markedly improves the efficiency of utilization of highly dispersed noble metals in pelleted catalysts, commonly reducing the amount of metal required for a given conversion by 50 percent or more, as compared to the use of conventional low pore volume carriers.

It will thus be understood that the efficient utilization of noble metal in the present catalysts is a synergistic function of both the carrier and the ion exchange technique employed to obtain highly dispersed metal. The high pore volume carriers offer little advantage over conventional low pore volume support if the degree of metal dispersion thereon is less than about 20 percent (on the basis of equal metal contents). The improved results shown herein hence require both a high pore volume, large pore diameter carrier, and the higher degree of metal dispersion obtainable by ion exchange, this preferably exceeding 30 percent.

Thus, the present invention provides a pelleted catalyst composition having a high activity for the hydrogenation of aromatic hydrocarbons, which comprises:

(1) a carrier composite of micelles of silica-alumina cogel dispersed in a large-pore high pore volume alumina gel matrix, the composite carrier having an ion exchange capacity of from 0.01 to 0.5 meq/g, a surface area of from 200 to 700 m²/g, and a pore volume of 0.8 to 2.0 ml/g, with 0.15 to

1.4 ml/g of said pore volume being in pores of diameter greater than 500 Å; and

(2) a minor proportion of a platinum group metal selectively dispersed by cation exchange on said silica-alumina cogel from an aqueous solution of a platinum group metal compound wherein the platinum group metal appears in the cation.

Detailed Description of Preferred Embodiments

A. Alumina-Silica Carriers

As will be apparent from the foregoing, the two critical requirements of the carriers employed herein relate to the ion-exchange capacity thereof (an indicia cracking activity), and the pore volume and pore size characteristics thereof. The ion-exchange characteristics are a function both of the alumina-silica ratio, and the degree of interaction between the alumina and silica components. In general, it is necessary to control the Al₂O₃/SiO₂ ratios, and the degree of interaction thereof, so as to achieve a final composition having an ion exchange capacity of from 0.01 to 0.5, preferably from 0.04 to 0.35 meq/gm (as determined by ion-exchange with aqueous sodium chloride solution, followed by titration of the liberated HCl). The ion exchange capacity of conventional 85% SiO₂/15% Al₂O₃ cogel cracking catalysts generally ranges between 0.3—0.5 meq/gm.

Pure silica gel and pure alumina gel have ion exchange capacities of substantially zero as determined by sodium chloride exchange. The zeolitic properties of alumina-silica cogs hence result from the chemical interaction of the two components, and the degree of interaction as well as the Al₂O₃/SiO₂ ratios control the resulting ion-exchange capacity. Maximum interaction between the silica and alumina components is normally obtained by methods such as coprecipitation from aqueous solutions of sodium aluminate and sodium silicate, cogelation of mixtures of alumina hydrosol and silica hydrosol, and impregnation of alumina hydrogel with silica hydrosol. Mixing the preformed hydrogels of silica and alumina generally results in a lesser degree of interaction, which can however be improved by extended aging of such mixtures at elevated temperatures. If the degree of interaction is low, as in the case of mixed, separately preformed gels, or mixtures wherein the silica is intimately composited with only a portion, e.g., 1—25%, of the alumina, it is normally preferred to employ relatively high silica/alumina ratios, e.g., from 20/80—40/60 on a dry weight basis. Conversely, where the degree of interaction is greater, the preferred ratios range from 5/95—25/75.

The distribution of ion exchange sites in the composite support must be heterogeneous. A homogeneous distribution is ordinarily

obtained when the silica/alumina ratio is uniform throughout the micellar gel structure, resulting for example from conventional coprecipitation or cogelation techniques.

5 These homogeneous supports, wherein the necessary silica content is uniformly distributed, are difficult to prepare in the large-pore, low-bulk-density forms required herein. Pure alumina on the other hand can readily

10 be prepared in these forms, as for example by spray drying of hydrous boehmite. Hence, the form of the support used herein consists of large-pore high-pore-volume alumina gel matrix in which is dispersed small micelles

15 (e.g., 10—200 microns in size) of a silica-alumina cogel, which form is referred to herein as the "heterogeneous" support.

In the heterogeneous supports, the dispersed silica-alumina cogel may have a high silica-

20 alumina weight ratio, in the conventional cracking catalyst range if desired, e.g., from about 50/50 to 85/15. In fact the preferred catalysts are those containing from 10—50%, preferably from 20—40%, by weight of a

25 50/50—85/15 silica-alumina cogel dispersed in a high-pore-volume, large-pore alumina gel matrix. It has been found also that the dispersed silica-alumina cogel need not exhibit the large-pore structure required for the overall catalyst composite; the large pores

30 in the surrounding alumina matrix appear to adequately overcome diffusion limitations.

A surprising aspect of the heterogeneous supports (in which the silica is intimately composited with only a portion of the total

35 alumina content) is that the alumina matrix appears to moderate the cracking activity of the dispersed silica-alumina cogel. Another advantage of these compositions is that the noble metal component is selectively chemisorbed on the dispersed cogel component, the alumina matrix having substantially no ion

40 exchange capacity. The resulting compositions exhibit an apparently advantageous localized concentration of active hydrogenation centers on the dispersed silica-alumina

45 phase.

The desired overall physical characteristics of the carriers are summarized in the following

50 table:

TABLE 1
Preferred Physical Characteristics of Carriers

55		General Range		Most Preferred Range	
	Pore Volume, ml/g	0.8	2.0	1.0	2.0
	Bulk Density, g/ml	0.2	0.6	0.3	0.5
	Surface Area				
	m ² /g	200	700	300	600
60	m ² /ml	100	300	100	250
	Av. Pore Diameter, Å	50	150	70	130
	Pore Size Distribution, Percent of Pore Volume in Pores of Diameter Greater than:				
65	100 Å	20	80	25	70
	500 Å	15	60	20	50
	Pore Volume (ml/g) in Pores of Diameter Greater than:				
70	100 Å	0.25	1.2	0.4	1.0
	500 Å	0.15	1.4	0.3	1.0

Methods for the manufacture of alumina-silica carriers of the above nature are known in the art. One such method comprises aging alumina-silica cogels at a high pH of e.g.,

75 10—12 at elevated temperatures, normally in ammoniacal media. Steaming is also a well known method of increasing average pore size (but not of total pore volume). A suitable method for preparing the heterogeneous supports involves

80 first preparing a silica-alumina cogel cracking catalyst as described in U.S. Patent No. 3,210,294, then mulling and homogenizing the resulting hydrogel with excess alumina hydrogel, followed by spray drying of the resulting

85 mixture. In still another method, a high-silica cogel, or "graft copolymer", is first prepared by impregnating silica-hydrogel with an aluminum salt followed by precipitation of alumina gel with ammonia hydroxide.

90 The resulting composition is then washed, blended with additional alumina hydrogel, mixed thoroughly and homogenized, followed by spray-drying and re-mulling with added

water, after which the mixture is extruded into suitable pellets. Any other suitable method may be employed to obtain the desired pore structure and surface area characteristics.

- 5 Prior to addition of the noble metal, the carrier is preferably (though not necessarily) formed into pellets of the desired size, normally at least 1/32-inch in diameter. The term "pellets" is intended to include extrudates, prills, beads, or any other suitable granular form.

Addition of Noble Metal

- 15 In accordance with the preferred embodiment of the invention, the foregoing carriers are advantageously ion-exchanged with an aqueous solution of a complex tetrammino-hydroxide of one or more of the metals platinum or palladium, to incorporate the metal therein on the form of a complex cation, after which the exchanger pellets are drained, dried and calcined. The operative tetrammino-hydroxide compounds include the following:

Platinous tetramminohydroxide,
 $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$

- 25 Platinic hexamminohydroxide,
 $\text{Pt}(\text{NH}_3)_6(\text{OH})_4$

Palladous tetramminohydroxide,
 $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$

- 30 Palladic hexamminohydroxide,
 $\text{Pd}(\text{NH}_3)_6(\text{OH})_4$

- The above compounds (hereinafter termed "complex hydroxides") can be conveniently prepared by methods described in U.S. Patent No. 2,773,742. Use of the complex hydroxides is advantageous in directing the exchange of the complex metal cation into the acidic exchange sites associated with the silica component of the carrier, while at the same time the hydrogen ions exchanged out of the carrier react with the hydroxyl groups of the complex hydroxides to form water. When other complex metal compounds are employed wherein the metal appears in the cation, e.g., platinous tetramminochloride, hydrogen chloride is formed as a by-product of the exchange, resulting in lowering of the pH of the solution, contamination of the solution with extraneous anions, and incomplete exchange of noble metal. It is necessary in such cases to add sufficient base such as ammonium hydroxide to keep the pH of the solution above about 10. The complex hydroxide compounds however are strongly alkaline in themselves and will raise the pH of the exchange solution to 12 or more, so that it is unnecessary to add another base in order to obtain complete ion exchange. By using the complex hydroxides, a substantially quantitative exchange of metal into the carrier is obtained, and the exchange

occurs selectively at the exchange sites associated with the silica component of the carrier. 60

A surprising aspect of the present invention is the improved hydrogenation activity obtained by ion exchange with the complex metal hydroxides, as compared to catalysts wherein an equal degree of metal dispersion is obtained by other ion exchange procedures. For example, it has been found that the carriers of this invention can be exchanged with solutions of chloroplatinic acid (wherein the platinum appears in the anion) and after calcining, the resulting catalysts display substantially equal metal dispersion as is obtained with the complex hydroxides. It appears however that the chloroplatinic anion combines selectively with the alumina component of the carrier, resulting in a catalyst of substantially lower activity. 65 70 75

The concentration of complex metal hydroxide in the exchange solution can be adjusted according to the desired amount of metal to be placed on the carrier. Since the exchange is substantially quantitative, it is normally desirable to employ relatively dilute exchange solutions in order to facilitate uniformity of exchange throughout the carrier. It is generally desirable to employ solutions in the concentration range of 0.001–0.2 M, and to use 2–10 ml of such solutions per gm of carrier. The exchange is complete when hydrogen sulfide fails to discolor a small sample of the solution. Ordinarily the exchange is complete in less than 2 hours, but it may be desirable in some cases to allow the mixture to stand for several hours longer in order to permit uniform distribution of the exchanged metal throughout the pellets. 80 85 90 95

The exchanged catalyst pellets are drained from the spent exchange solution, dried at e.g., 200–250°F. for 3–4 hours, and then calcined if desired in dry air at temperatures of e.g., 600–1200°F. for about 6–20 hours. However, the calcination step is normally unnecessary. An optimum drying procedure consists in heating the catalyst in circulating air, or on a belt drier, at temperatures in the range of about 450–700°F., while maintaining sufficient air circulation to complete the drying in as short a time as possible, preferably about 30 minutes to 5 hours. It has been found that catalysts dried at 500°F. with sufficient air circulation to complete the drying in 5 hours are almost 50% more active than catalysts dried at the same temperature over a period of 8 hours. It has also been found that temperatures above about 500°F. are detrimental to catalysts which contain more than about 0.3 weight-percent of residual sulfate ions (from the aluminum sulfate used in the manufacture of the support). 100 105 110 115 120

Prior to use in the hydrogenation process, it is normally desirable to reduce the dried

and/or calcined catalyst in hydrogen at temperatures of e.g., 400°—1000°F. for several hours.

Desirable concentrations of noble metal in the finished catalysts range from 0.01 to 2 weight-percent, preferably from 0.1 to 1 percent.

As mentioned above it is preferred that the carrier should be pelletized prior to the addition of the noble metal. However, the addition of noble metal can precede the pelletization step.

Hydrogenation Conditions

The hydrogenation conditions employed herein are substantially conventional, with the exception that the very high activity of the catalyst often permits the use of higher space velocities and/or lower temperatures than are normally employed. Under the preferred conditions of temperature, pressure and feedstocks, the operation is substantially liquid phase; the preferred mode of operation being a conventional fixed bed type wherein the feed plus hydrogen is preheated and passed downwardly through one or more beds of the catalyst. Preferred hydrogenation conditions are summarized as follows:

TABLE 2
Preferred Hydrogenation Conditions

	General Range	More Preferred Range
Temperature, °F.	300—700	400—650
Pressure psig	150—2000	400—1500
LHSV	1—20	2—12
H ₂ /Oil, MSCF/B	3—20	5—12

Those skilled in the art will readily understand that the above conditions are suitably correlated to effect the desired degree of hydrogenation with reference to the particular feedstock. Normally, it is also desirable to correlate temperature and space velocity to minimize cracking, specifically to avoid converting more than about 1 percent of the feed to products boiling below the initial boiling point of the feed.

Feedstocks

The process may be applied advantageously to the hydrogenation of substantially any individual aromatic hydrocarbon, mixtures thereof, or mineral oil fractions boiling in the range of about 100°—1000°F. Benzene may be converted to cyclohexane, and toluene to methylcyclohexane. Preferred feedstocks comprise mineral oil fractions boiling in the solvent naphtha, turbine fuel or diesel fuel ranges, and which normally contain up to 50—60 volume percent of aromatic hydrocarbons. Specifically contemplated feeds comprise solvent fractions boiling in the range of 300°—400°F., and turbine fuel fractions

boiling in the range of 350°—500°F. The process may be advantageously applied to reduce the aromatic content of such feeds to below 5 volume percent, and below 1 percent if desired.

Another advantageous feature of the catalysts of this invention is their increased tolerance to sulfur. As is well known, most noble metal catalysts are poisoned by sulfur compounds, but it is found that the present catalysts can be advantageously utilized to hydrogenate feeds containing from 10—100 parts per million of sulfur or more.

The following examples are presented to illustrate the invention.

EXAMPLE I

A preferred catalyst (designated catalyst "A") of the present invention was prepared as follows:

A solution of tetraamminoplatinous chloride was prepared by dissolving 5.4 gms of Pt(NH₃)₄Cl₂·H₂O in 2000 ml of deionized water, and the resulting solution was percolated downwardly through a 500 ml bed of freshly regenerated (hydroxide) Amberlite IRA-400 resin at the rate of 100 ml/minute. The bed was then flushed with 500 ml of deionized water and the wash water was combined with the main 2000 ml of solution, to which was also added 25 ml of 28% NH₃ solution.

To the resulting 0.006 M solution of Pt(NH₃)₄(OH)₂ was then added 500 gms of a freshly calcined, extruded (1/16-inch) 80% alumina—20% silica heterogeneous cogel carrier prepared by mulling about 27 parts by dry weight of a 75/25 silica-alumina "graft copolymer" (alumina precipitated via aluminum sulfate solution into the pores of a preformed silica gel) with 73 parts by dry weight of hydrous alumina gel, followed by spray drying, rehomogenization with added water, and extrusion. The resulting carrier had the following properties after calcination at 600°C.

TABLE 3

Pore Volume, ml/g	1.19	
Bulk Density, g/ml	0.40	
Surface Area, m ² /g	352	110
m ² /ml	141	
Percent Pore Volume in Pores of diameter Greater than:		
1,000 Å	30.5	115
500	36.4	
100	51.3	
Pore Volume (ml/g) in Pores of Diameter Greater than:		
1,000 Å	0.36	120
500	0.43	
100	0.61	
Ion Exchange Capacity, meq/g	0.24	

The resulting mixture was shaken gently every 5—10 minutes over a period of about 2 hours, and then allowed to stand for 12 hours. The spent exchange solution was free of platinum. The exchanged pellets were then drained, dried at 110°C. for about 3 hours and calcined in dry air at 480°C. for 12 hours. The resulting catalyst contained 0.56 weight-percent Pt in a state of 43% dispersion, and had a bulk density of 0.40 g/ml.

EXAMPLE II

Another, relatively non-preferred catalyst (designated "B") of the present invention was prepared substantially as described in Example I, utilizing as the carrier an intermediate pore volume, extruded, 80% alumina—20% silica heterogeneous cogel carrier prepared as described in Example I, except that a lower pore volume alumina gel was employed, the resulting composition having the following characteristics:

TABLE 4

	Pore Volume, ml/g	0.96
	Bulk Density, g/ml	0.50
25	Surface Area, m ² /g	487
	m ² /ml	239
	Percent Pore Volume in Pores of Diameter Greater than:	
30	1000 Å	23.4
	500	25.0
	100	32.3
	Pore Volume (ml/g in Pores of Diameter Greater than:	
35	1000 Å	0.225
	500	0.24
	100	0.31

Ion Exchange Capacity, meq/g 0.3

The resulting catalyst contained 0.573 weight-percent of Pt in a state of 32 percent dispersion, and had a bulk density of 0.50 g/ml.

EXAMPLE III

For purposes of comparison, another catalyst, "C", was prepared, using the same high pore volume carrier of Example I, but wherein the platinum was added by impregnation and/or ion-exchange with an aqueous solution of chloroplatinic acid (H₂PtCl₆). The resulting catalyst contained 0.463 weight-percent Pt in a state of 59 percent dispersion, and had a bulk density of 0.45 g/ml.

EXAMPLE IV

For further comparison, a highly active commercial reforming catalyst (designated "D") containing 0.55 weight-percent Pt (48 percent dispersion) impregnated via chloroplatinic acid on a mixed, eta-gamma alumina

carrier was obtained, and its pore characteristic determined as follows:

TABLE 5

	Pore Volume, ml/g	0.51
	Bulk Density, g/ml	0.765
	Surface Area, m ² /g	372
	m ² /ml	284
	Percent Pore Volume in Pores of Diameter Greater than:	
	1000 Å	13.1
	500	25.3
	100	39.0
	Pore Volume (ml/g) in Pores of Diameter Greater than:	
	1000 Å	0.077
	500	0.13
	100	0.20

EXAMPLE V

Each of the foregoing catalysts was then tested for hydrogenation activity, using as the feed a hydrofined petroleum jet-fuel fraction having the following characteristics:

	Gravity, °API	39.2
	Boiling range, Engler D-86, °F.	
	Initial	288
	10%	311
	50%	390
	Max	548
	Nitrogen, ppm	0.3
	Sulfur, ppm	4.0
	Volume-Percent:	
	Aromatics	36
	Olefins	0
	Saturates	64

Hydrogenation conditions were as follows:

	Temperature, °F.	500
	LHSV	8
	Pressure, psig	600
	H ₂ /Oil MSCF/B	6

The significant results of the test runs were as follows:

TABLE 6

	Vol-% Aromatics in Product			
Catalyst	A	B	C	D
Hours on Stream				
18	2.2	5.1	6.5	5.7
30	2.7	4.8	7.8	6.8
42	3.0	5.4	9.8	8.0
54	—	5.6	11.0	9.0
66	—	6.3	11.6	10.0
78	—	6.4	10.5	10.8

Assigning an arbitrary activity of 100 to Catalyst D for each portion of the run, the

relative volume activities of the respective catalysts are as follows:

TABLE 7					
Relative Volume Activities					
5	Catalyst A	B	C	D	
Hours on Stream					
18	256	111	87	100	
30	253	141	87	100	
10	42	267	148	82	100
54	—	160	82	100	
66	—	159	86	100	
78	—	168	103	100	

The foregoing volume activities do not however reflect the efficiency of utilization of the platinum content of the respective catalysts. Some indication of this factor can be obtained by dividing the foregoing activities by the weight of platinum per 100 ml (determined by multiplying weight-percent Pt times bulk density), of the respective catalysts, giving the following figures for relative efficiency of platinum utilization:

TABLE 8				
Relative Efficiency of Platinum Utilization				
25	Catalyst A	B	C	D
Hours on Stream				
18	1142	383	415	227
30	1130	486	415	227
42	1192	510	390	227
54	—	550	390	227
66	—	548	410	227
78	—	580	490	227

From the foregoing it is apparent that the high pore volume catalysts A, B, and C are much superior to the conventional low pore volume catalyst D. Catalyst C, prepared by impregnation with chloroplatinic acid, was initially about equal in volume activity to catalyst B (prepared according to the present invention), but deactivated much more rapidly. The marked superiority of high-pore-volume catalyst A over intermediate-pore-volume catalyst B is also readily apparent. In all of the foregoing runs, there was less than 1 percent conversion to produce boiling below the initial boiling point of the feed.

EXAMPLE VI

To demonstrate the superior sulfur tolerance of the catalysts of this invention, two parallel runs were carried out using a sulfur-containing solvent naphtha feed having the following characteristics:

55	Gravity, °API	49.8
	Engler Distillation	290—386 (IBP/Max)
	Sulfur, ppm	73
	Aromatics, Vol-%	19
60	Saturates	81

Conventional catalyst D described above was compared with a high pore volume catalyst E, which was essentially identical to catalyst A above, except that the Pt content was 0.6 weight-percent and its pore volume was 1.43 ml/g (bulk density=0.37 g/ml).

Process conditions were selected to achieve substantially complete initial aromatics saturation with each of the fresh catalysts as follows:

Temperature, °F.	600	
Pressure, psig	1100	
LHSV	2.3	
H ₂ /Oil, MSCF/B	5430	75

Over the 700-hour run, aromatics saturation remained substantially complete with catalyst E, but declined with catalyst D, as follows:

TABLE 9			
Vol-% Aromatics in Product			
Hours on Stream	Catalyst E	Catalyst D	
0	0.1	0.2	
100	0.1	0.5	85
200	0.0	0.9	
400	0.0	2.5	
600	0.0	3.5	
700	0.0	3.8	

The superior sulfur-tolerance of catalyst E is readily apparent.

EXAMPLE VII

To demonstrate the effect of silica content, another catalyst was prepared essentially as described in Example I, with the exception that the proportion of 75/25 silica-alumina "graft-copolymer" was halved, resulting in a final composition containing 10 weight-percent SiO₂ and having an ion exchange capacity of 0.13 meq./g. An aromatics hydrogenation test run showed that this catalyst had only about 60% of the activity of the 20% SiO₂ catalyst of Example I.

EXAMPLE VIII

A homogeneous, 20% SiO₂—80% Al₂O₃ cogel base was prepared by conventional methods, and after extruding, drying and calcining was found to have the following properties:

TABLE 10		
Pore Volume, ml/g	1.20	110
Bulk Density, g/ml	0.42	
Surface Area, m ² /g	385	115
m ² /ml	161	

TABLE 10 (continued)
Percent Pore Volume in Pores
of Diameter Greater than:

5	1000 Å	10.8
	500	16.7
	100	44.0
Pore Volume (ml/g) in Pores of Diameter Greater than:		
10	1000 Å	0.13
	500	0.20
	100	0.52
Ion Exchange Capacity, meq/g		0.195

After adding 0.57 weight-percent of Pt as described in Example I, the resulting catalyst had a Pt dispersion of 57 percent, but was found to be only about 85 percent as active for hydrogenation as the catalyst of Example I, thus showing that the lack of sufficient pore volume in the >500 Å size range prevents full utilization of the active centers in the catalyst. It is apparent that adequate silica content, ion-exchange capacity, and Pt dispersion are not alone sufficient to give the desired bulk volume activity.

25 WHAT WE CLAIM IS:—

1. A pelleted catalyst composition having a high activity for the hydrogenation of aromatic hydrocarbons, which comprises:

(1) a carrier composite of micelles of silica-alumina-cogel dispersed in a large-pore high pore volume alumina gel matrix, the composite carrier having an ion exchange capacity of from 0.01 to 0.5 meq/g, a surface area of from 200 to 700 m²/g, and a pore volume of 0.8 to 2.0 ml/g, with 0.15 to 1.4 ml/g of said pore volume being in pores of diameter greater than 500 Å; and

(2) a minor proportion of a platinum group metal selectively dispersed by cation exchange on said silica-alumina cogel from an aqueous solution of a platinum group metal com-

pound wherein the platinum group metal appears in the cation.

2. A catalyst composition as defined in claim 1, wherein said platinum group metal compound is selected from platinous tetramminohydroxide, platonic hexamminohydroxide, palladous tetramminohydroxide, and palladic hexamminohydroxide.

3. A catalyst composition as defined in claim 1 or claim 2, wherein said silica-alumina cogel has a SiO₂/Al₂O₃ weight ratio of 50/50 to 85/15, and comprises 20 to 40 weight-percent of the composite carrier.

4. A catalyst composition as defined in any preceding claim, wherein the ion exchange capacity of said carrier composite is from 0.04 to 0.35 meq/g.

5. A catalyst composition as defined in any preceding claim, wherein said carrier composite has the physical characteristic set forth in the final column of Table 1 herein.

6. A catalyst composition as defined in Claim 1 and substantially as hereinbefore described.

7. A process for the hydrogenation of an aromatic hydrocarbon feedstock, which comprises contacting said feedstock at a temperature of from 300° to 700°F. and at an elevated pressure in the presence of added hydrogen with a catalyst composition as defined in any preceding claim.

8. A process as defined in Claim 7, wherein hydrogenation conditions are as set forth in the final column of Table 2 herein.

9. A process for the hydrogenation of an aromatic hydrocarbon feedstock as defined in Claim 7 and substantially as hereinbefore described.

10. A hydrocarbon feedstock which has been hydrogenated by a process as defined in any one of Claims 7—9.

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